Structure of Protein Fibers*

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NATURAL organic textile fibers belong to only two compositional groups—the cellulosic group, represented by such fibers as cotton, flax and jute, and the protein group, represented by wool, mohair and silk. With each fiber are associated characteristic properties which recommend as well as limit it to particular uses. Cotton, and cellulose fibers in general, possess high strength, low extensibility, and good water resistance; wool is valued for the warmth, resilience, crease- and crush-resistance of its fabrics, while silk possesses both considerable strength and resilience and is unique among the natural fibers in that it occurs as a continuous filament.

Because silk was an expensive and relatively scarce fiber, the first experiments, made about a century ago, were directed toward producing an artificial fiber with the properties of silk. Curiously, this work resulted in the production of rayon, regenerated cellulosic fiber rather than a regenerated protein fiber. The first rayons produced were weak, particularly when wet, and were considered by many to be an ephemeral invention. Today rayons are available in a great range of strengths and elongations—the high-tenacity viscose and saponified acetate fibers are now produced with strengths of 6 to 9 grams per denier, strengths once considered impossible to achieve. Even though the rayons far exceed silk and wool in strength, they fail to replace these fibers in many fabrics. Silk is preferred for hosiery and sheer dress goods, wool for suits, blankets and carpets. The property of silk and wool largely responsible for their use in these materials is the ability to recover from large deformations, whether produced by stretching, twisting or crushing.

Since all proteins are alike in that their molecules have the same basic structure, the polypeptide chain, it would appear that some of the non-fibrous proteins might well be modified to make a silk- or wool-like fiber. This idea is not new, for patents appeared about 1900 describing methods of spinning casein, the protein of milk, into fibers. It was not until the last decade, however, that artificial protein fibers appeared on the market both here and abroad. These fibers, known as Lanital in Italy, Lactofil in the Netherlands and Aralac in this country, are spun from casein. Experimental work has been reported on fibers from many other proteins—chief among these are the proteins of peanuts, soybeans, corn, egg white and feathers. Ardil, a fiber from peanut protein, is being produced on a pilot-plant scale in England.

Whereas the artificial protein fibers, as presently produced, are not outstandingly strong, they are resilient and are similar in many respects to the natural protein fibers. It is desirable to examine in some detail the structures of the natural protein fibers as well as the artificial fibers to find which aspects of these structures contribute importantly to their macroscopic physical properties.

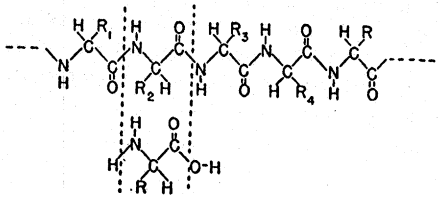
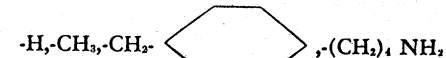


Figure 1. A generalized polypeptide chain. Dotted lines enclose an α-amino-acid residue which is the repeating unit of the chain.

Fundamentally, textile fibers are made up of threadlike molecules of high molecular weight, and protein fibers are no exception to this rule. Symbolically, the polypetitide chain may be represented as in Figure 1. The monomer of this righ polymeric molecule is the α-amino-acid residue, one of which is enclosed by the dotted lines in Figure 1. In contrast to most other high polymers, the polypetide chain is not built by repeating a single monomer or a combination of two or three different monomers, but is a complicated copolymer built from many different monomers. It is true that all the monomers are α-amino acids, but they differ in the nature of the side group R, which may be



-H, -CH_3, -CH_2- ⟨⬡⟩ , -$(CH_2)_4$ NH_2

-CH_2, -CH_2-COOH, etc., in all, some twenty-five different amino acids have so far been isolated from proteins. The properties of any protein or the fiber derived from it must depend on its amino-acid composition, on the arrangement or sequence of the different amino-acid residues along the polypetide chain, the length of the chain, and the spatial configuration of the chain—whether it is extended as a threadlike molecule or is folded into a more or less compact ellipsoidal particle. In any protein fiber, natural or artificial, some of these factors can be changed in moderate degree by chemical or physical treatment. Minor changes in composition of the fiber can be effected by reaction of the side groups R with various small molecules; this is the basis of the hardening or tanning treatments applied to leather and artificial protein fibers, and of the shrink-proofing of wool. Chain length, an important factor in any textile fiber, unfortunately can be varied only in one direction, and that is downward. The arrangement or sequence of the various amino acids along the polypeptide chain of a given protein is inflexible. Only by hydrolysis of the protein into its constituent amino acids and by recondensation into a high polymer could the sequence be affected; at present this process is not feasible. The last consideration, that of the degree of extension or folding of the molecular chains, is directly related to the mechanical properties exhibited by the fibers. It is of primary importance in the artificial protein fibers, for the most abundant source of material for these fibers is the globular proteins whose molecules are composed of polypeptide chains coiled or folded into compact, near-spherical particles, which in this configuration are not suited to fiber formation. To make a fiber of maximum strength, these molecules must be unfolded and arranged with the prevailing direction of their long axis along the fiber axis, much in the manner that a yarn is spun by arranging the individual filaments into a more or less parallel bundle.

A comparison of the structure of silk, wool, collagen, and some artificial pro-

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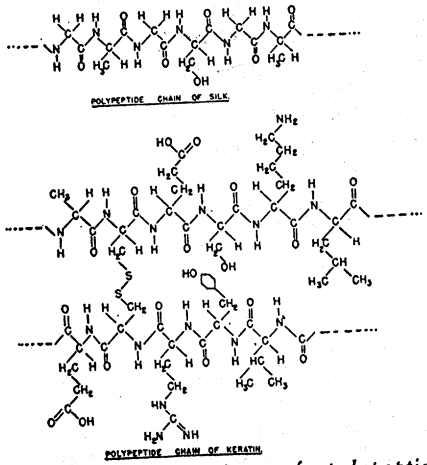

Figure 2. Comparison of polypeptide chains of (a) silk and (b) wool.

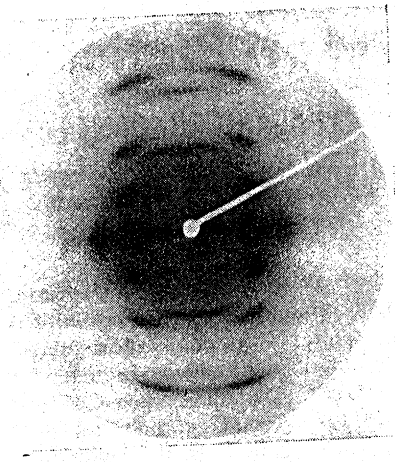

Figure 4. Diffraction pattern of silk.

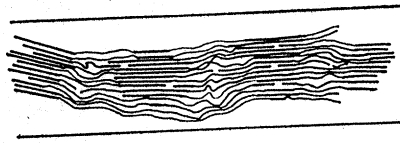

Figure 5. Schematic representation of the amorphous and crystalline regions in a fiber. Heavy straight lines represent chain in a crystalline area (after Mark.)

tein fibers, their composition and physical properties, will serve to illustrate the influence of some of the factors we have mentioned.

Silk

We shall first consider silk. Among the protein fibers, silk is the strongest, its tensile strength ranging from 3.5 to 4.5 grams per denier. Combined with this high strength it has a moderate degree of extensibility, elongating ten to fifteen per cent before breaking. Compositionally, silk is set apart from all other proteins owing to its high content of the simple amino acids, glycine and alanine, these two acids comprising about 75 per cent of the residues in the polypeptide chains. Serine and tyrosine each constitute another 10 per cent of the polypeptide chain. Thus the major part of the molecule is accounted for. In Figure 2 the polypeptide chain of silk is compared with that of wool. The side groups R of glycine and alanine are -H and -CH_3 respectively; both are small groups, and since they account for the majority of the side groups of the molecule, the extended polypeptide chain presents a relatively smooth surface, and it may be expected to pack well with its neighbors. Figure 3 is a photograph of scale models of the polypeptide chains of silk and wool and more accurately illustrates the differences in the distribution of matter along the chains.

Direct information concerning the arrangement of the polypeptide chains in silk is gained by a study of its X-ray diffraction pattern, which is presented in Figure 4. For any substance to produce such an X-ray pattern requires that there be a regular, periodic arrangement of its atoms and molecules, an approximation to the spatial order associated with an obviously crystalline substance such as sucrose. Clearly, the entire silk fiber cannot constitute a single crystal, for if this were true, the fiber would be brittle and have very low extensibility, much like asbestos. We are then led to the concept of a fiber composed of crystalline regions interposed with amorphous regions as represented in Figure 5. The amorphous regions contribute mainly to the hazy background of the X-ray diffraction pattern. A molecular chain may run through several such crystalline and amorphous regions. It is the amorphous regions, then, where the chains are less tightly packed and more or less kinked, that allow the fiber to flex and extend moderate amounts without permanent deformation. From this reasoning, it is to be expected that the flexibility and elongation of a fiber will depend upon the relative extent of crystalline and amorphous regions, the fiber becoming less extensible as the proportion of crystalline material increases. Another factor to be considered is the orientation of the molecular chains with respect to the fiber axis. Since primary bonds within a molecule are much stronger than the secondary bonds between molecules, rupture of a fiber occurs mainly as a result of slippage of molecular chains. If the chains all run in the direction of the fiber axis, then the lateral interactions along the considerable length of the molecules must be overcome simultaneously in order to separate them from their neighbors. If the direction of the molecular chains is transverse to the fiber axis, then on application of stress the chains will tend to separate by a zipper action, in which the fracture is propagated by successive rather than simultaneous rupture of lateral bonds along the chains. Consequently, we may expect the tenacity of a fiber to increase as preferential orientation of the molecules in the fiber direction increases. Tenacity should also increase with the chain length or molecular weight for this increases the average number of secondary bonds that must be broken in order to separate one molecule from its neighbors. Orientation is to be distinguished from crystallinity for it refers only to the

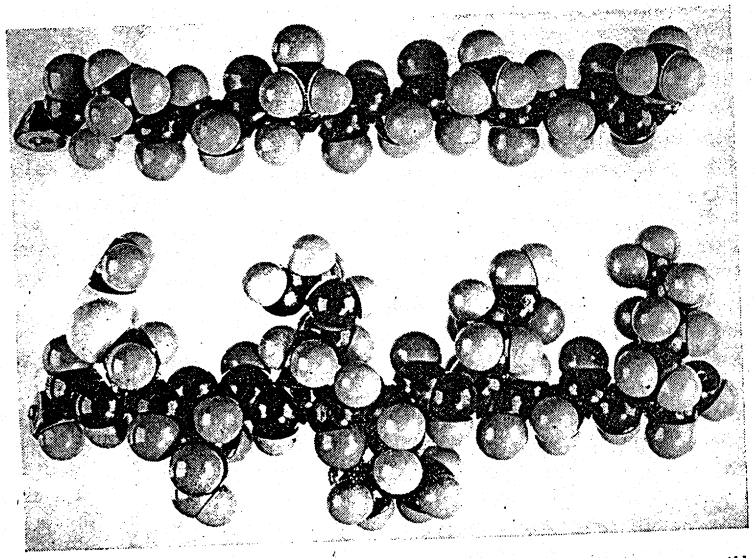

Figure 3. Photograph of scale models of polypeptide chains of a silk (above) and wool.

irection of the molecular chains, whereas ystallinity refers to the perfection of packing of the molecules in all directions. Thus a highly crystalline fiber may not ossess orientation, and the converse is also true. Unfortunately, the discrete diffraction pattern of a fiber reflects only the rientation and arrangement existing in ie crystalline regions, and we must employ less direct methods to investigate the less ordered or amorphous regions.

Compared to other protein fibers, both natural and artificial, silk is not only highly oriented but is the highest on the crystallinity scale. It also shows the lowest swelling when immersed in water and lowest absorption from the vapor phase. The relationship of these observations is explained by the X-ray evidence, to be described later, that the crystalline portions are not penetrated by water. Although the amorphous portions of silk probably take up as much water at normal humidities as the corresponding regions in other protein fibers,[1] their proportion is less and consequently the overall absorption is decreased. Impermeability of the crystalline regions by water permits relatively large portions of each polypeptide chain to be held firmly in the fiber structure, even though other portions of the chain are separated from neighboring silk molecules by water molecules. High tensile strength is thus maintained even in the wet state.

The position of the spots on the diffraction pattern of silk gives a measure of the arrangement and packing of the molecular chains. To make this statement more clear, let us consider the diffraction of X-rays by a set of polypeptide chains composing a portion of a "crystallite" present in a silk fiber, as illustrated by Figure 6. The atoms are considered to lie in sets of parallel layers both horizontally and vertically, as indicated by the planes drawn in the figure. Each layer behaves like a mirror toward the incoming beam of X-rays, reflecting them continuously as the crystallite is rotated about the vertical axis. Each set of planes then gives rise to a streak across the X-ray film. However, since all layers of a set are illuminated simultaneously by the X-ray beam, destructive interference occurs among the reflected beams, causing neutralization at all angles except one (the Bragg angle), which depends on the separation between the layers. The diffraction pattern of a rotating crystallite thus consists of a set of discrete spots due to the various sets of atomic layers. From the position of the spots we can calculate the distance between the layers and also the angle of inclination of the layers with respect to the axis perpendicular to the X-ray beam.

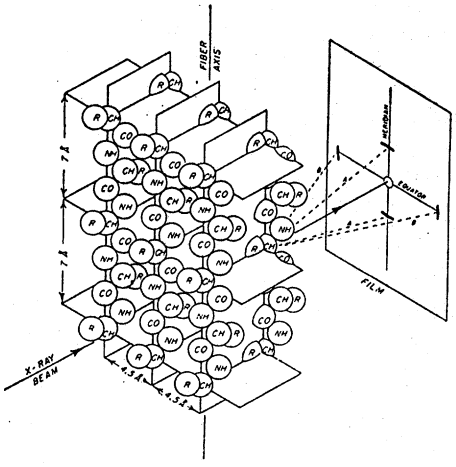

Figure 6. Diffraction of X-rays by a silk crystallite (reproduced from "The Chemistry of Leather Manufacture" by George D. McLaughlin and Edwin R. Theis, American Chemical Society Monograph published 1945 by the Reinhold Publishing Corp., New York).

Interestingly, a silk fiber, or any other textile fiber, need not be rotated in an X-ray beam to produce its diffraction pattern. This is clear evidence that it is a polycrystalline substance, with all the crystallites having one axis along the direction of the fiber, but some of them rotated about this axis so that one set of atomic layers is in position to reflect, while oher crystallites are in reflecting position for other sets of planes. Any deviation of the axis of the crystallites from the fiber axis results in a broadening of the diffraction spots into arcs. The X-ray photograph thus gives a measure of the inclination or "orientation" of the crystallites, and therefore the molecular chains, with respect to the fiber axis.

From the meridian reflections, we calculate that the spacing between planes perpendicular to the fiber axis is 7 Ångstrom units (Å). This is very close to the distance computed for two residues of a fully extended polypeptide chain, assuming the bond distances and angles found in small molecules. It is therefore evident that the polypeptide chains are in their fully extended configuration in the crystallites and that the long axis of the molecular chains runs along the fiber axis.

The reflections on the equator of the X-ray pattern are a measure of the lateral spacing of the polypeptide chains. These are the spacings which would be expected to change if water penetrated the crystallites and forced the chains apart. Patterns of wet silk fibers are identical with those given by fibers at normal humidities. It follows that water has not entered the portion of the fiber responsible for the X-ray pattern.

Wool

Wool provides an interesting comparison with silk. Its dry strength ranges from 1 to 1.6 grams per denier, values low compared to silk; but like silk, little strength is lost on immersion in water, although for an entirely different reason. It is further distinguished from silk by its high reversible extensibility. This is especially apparent in the wet state. A wet wool fiber can be extended sixty per cent and upon release it immediately returns to its original length. At normal humidities this property of rapid recovery from deformation is manifest in the resilience of wool and makes for crease-resistant and crush-resistant fabrics.

As shown in Figure 2, the composition of wool results in a polypeptide chain with a very rough surface compared to that of silk. In wool we have 5 per cent of glycine and alanine, 22.5 per cent aspartic and glutamic acids, 10 per cent arginine, 11.5 per cent leucine and isoleucine, about 12 per cent cystine, and amounts of at least nine other amino acids sufficient to account for 85 per cent of the keratin molecule. Very important to the properties of wool is its high content of cystine, which forms sulfur bridges between adjacent polypeptide chains and binds the wool fiber into giant molecular aggregates.

In the normal state, wool gives the X-ray diffraction pattern reproduced in Figure 7. This has been called the "α-keratin" pattern by Astbury.[2] Compared to silk, this pattern signifies a low order of crystallinity in the fiber, both as to perfection and amount. An important feature of the pattern is the reflection

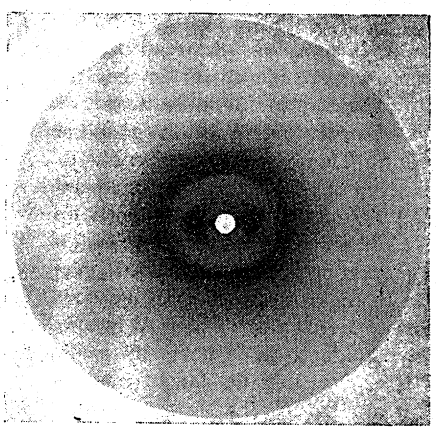

Figure 7. Diffraction pattern of unstretched wool, α-keratin structure.

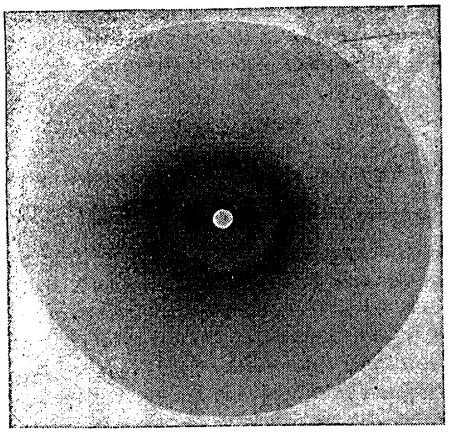

Figure 8. Diffraction pattern of stretched wool, β-keratin structure.

occurring on the meridian, which shows that the repeat period along the polypeptide chain is 5.1 Å as compared to 7 Å in silk. A single amino-acid residue extends 3.6 Å, and two residues in their most extended configuration project 7.2 Å on the fiber axis; to satisfy a repeat period of 5.1 Å it appears that the polypeptide chain must be regularly folded, with two or more amino-acid residues occurring in each fold of the chain.

If wool is stretched 20 to 100 per cent the X-ray pattern transforms to the "β-keratin" shown in Figure 8. A new set of reflections occurs corresponding to a fiber repeat period of 6.7 Å, or more nearly that required by a fully extended polypeptide chain. This transformation is reversible. If the stretched fiber is released in water, it returns almost to its initial length and it gives the original X-ray pattern. The reversible extensibility of wool at extensions greater than 20 per cent is thus associated with a reversible unfolding of the polypeptide chains in the organized portions of the fiber. Thermal-stress data[3] indicate that the elasticity at extensions below 20 per cent is due to a similar mechanism—the tendency of the partially extended chains in the less organized portions to return to a specific folded configuration of lower potential energy. This is to be contrasted with the elasticity of rubber which results from the tendency of the extended polymer chains to kink and coil in a random fashion. It is interesting that the extended polypeptide chains in stretched wool are not in a stable state as they are in silk where the polypeptide chain is normally extended. It is evident that the lateral interactions between the chains, arising from the cystine cross-bonding as well as secondary bonding by hydrogen bridges and polar attractions, are not sufficient to resist the contractile tendency of the system. The cystine cross-bonds may, in fact, favor the folded configuration for if the folds in adjacent chains between successive cystine cross-bonds differ considerably in length, then the system is not permitted to transform entirely into stable extended chain structure. If stretched wool is steamed so that some of the cystine bridges are broken, rearranged spatially, and reformed as the same or another type linkage, a β-keratin configuration results. The process is commonly referred to as "permanent set."

It becomes apparent, too, that the cystine linkages are in large measure responsible for the high wet strength of wool. Water swells wool considerably, plasticizing or lubricating the molecules and permitting them to move readily with respect to each other—but only up to a certain limit. When this limit is reached, at about 100 per cent extension, the full stress is applied to the cross-bonds, which prove to be nearly as strong as all the lateral bonding operative in the dry filaments. If the cystine bonds are broken chemically and not reformed, then wool decreases greatly in wet strength and shows only slight resistance to extension when wet.[4] The dry strength, however, is only slightly affected, showing that the secondary attractions between long chain molecules are sufficient to impart considerable strength.

Collagen

Classified according to their X-ray diffraction pattern, the keratins of wool and hair, and the fibroin of silk fall into the same group, for both are built of polypeptide chains which, when extended, show a fiber repeat period of about 7 Å. On the same basis collagen belongs to a different group of fibrous proteins, since its diffraction pattern (Figure 9) gives a

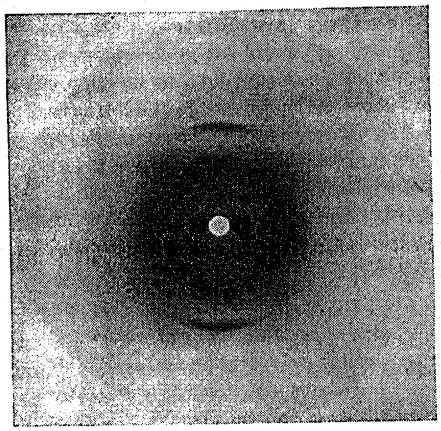

Figure 9. Diffraction pattern of oriented collagen.

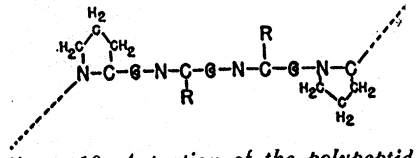

Figure 10. A portion of the polypeptide chain of collagen showing the effect of the proline residues on the direction of the polypeptide chain. The chain is viewed parallel to the plane containing the main-chain bonds of the amino-acid residues. In Figures 1 and 2 the chain is viewed perpendicular to this plane.

repeat distance along the polypeptide chain of 8.4 Å. Like silk, this feature of the X-ray diagram is unaffected by stretching or relaxing the fibers. The molecular arrangement remains the same in the organized portions of the fiber. Only the orientation and total amount of these regions change.

Again we turn to the analytical data for a clue to this new X-ray pattern. The data indicate that about one-third the residues in collagen are glycine, somewhat less than one-third are proline or hydroxyproline, one-ninth are alanine, one-twentieth are leucine, and the greater proportion of the remaining amino-acid residues have polar side groups. It is the high content of proline and hydroxyproline which most likely accounts for the structural difference between collagen and silk or wool. This is because of the peculiar configuration of proline, as indicated in Figure 10.

At each proline residue there is a -C-N- linkage which constitutes part of the main chain but about which there cannot be free rotation since this linkage is also part of a five-membered ring. If a segament of a polypeptide chain is in its most extended form, and if this segment includes the -C-N- bond of proline, it is to be noted, as shown in Figure 10, that the succeeding -N-C- bond is deviated markedly from the plane containing the main chain bonds of the other residues. It follows that an extended polypeptide chain such as found in silk or stretched wool is not possible for collagen. For a polypeptide chain, in which proline occurs at frequent intervals, to repeat itself regularly and continue along a generally straight line, it must take some folded form[5] or spiral form[6] in which each amino acid residue projects 2.9 Å on the fiber axis. Because of the restrictions imposed by the proline residues an average projection of 2.9 Å per residue also represents a collagen molecule at near maximum extension. Hence, it is not surprising that stretching collage does not change the fiber repeat period. Neither would we expect oriented col-

;en to exhibit long range elasticity simi- to that shown by wool. Any elongation on stressing must result from the straightening out of kinked chains or from ppage of chains in the amorphous portions of the fiber.

Collagen swells much more in water in either wool or silk, absorbing roughsix times as much water as wool and nine times as much water as silk. It might be expected that the hydrophilic character of a protein is related to the number of polar side groups along the polypeptide chain, but in this respect collagen and wool are not greatly different; the much lower swelling of wool must then be due to some difference in the structural organization of the fiber which resists chain separation. The cystine cross-linkages occurring between adjacent chains every tenth amino-acid residue in wool would serve this function by tying the chains together in a reticular structure which effectively resists swelling. Collagen contains only minor amounts of cystine, less than 0.2 per cent, and primary cross-linking of this kind must be infrequent. In this connection it is interesting that while collagen swells considerably in water relative to wool or silk, this swelling is still definitely limited by the structure. If the collagen molecules are somewhat degraded, as in the formation of gelatin, water-soluble product results, even though the molecular weight may be 100,000. Whether the limited swelling of collagen is due to the presence of a few linkages between adjacent chains or to its high molecular weight cannot be stated. Even so, native collagen is ordinarily chemically treated to reduce its hydrophilic character, and this is a principal object in the tanning operation.

Thus far we have spoken only of short-range periodicity—5 or 10 Angstrom units—assignable to lateral separation and to recurrence of short loops in threadlike molecules, and to regular repetition of amino-acid residues in a polypeptide. Keratin,[7] silk,[8] and collagen all show a further, long-range periodicity, not yet satisfactorily explained. The fundamental spacing in collagen is 640 Å nd was discovered by its diffraction effects.[9]. It has been revealed also through electron microscopy by Schmitt and his collaborators.[10]

Collagen is easily dispersed into submicroscopic fibrils, characteristically striated transversely. Micrographs of collagen fibrils, made in this Laboratory durg an electron microscopic study of the ects of leather manufacturing procedures on collagen primary structures, are reproduced as Figures 11 and 12. Figure 11 shows a group of fibrils at magnification 30,000 X. The three-dimensional aspect arises in shadows cast by oblique deposition of gold upon the specimen. The uniform repeat distance of 640 Å is evident, and it is clear that the striated appearance is due to a succession of duplex ridges separated by shadowed depressions along the fibril. Long-range periodicity is displayed further resolved in Figure 12, in which the magnification is 200,000 X. Two fibrils of opposite polarity are shown in close lateral association. Each fibril is only about 800 Å across. The larger intervals drawn at the right mark off the 640 Å period, and shorter lines are directed toward six sub-units. These are not equally spaced.

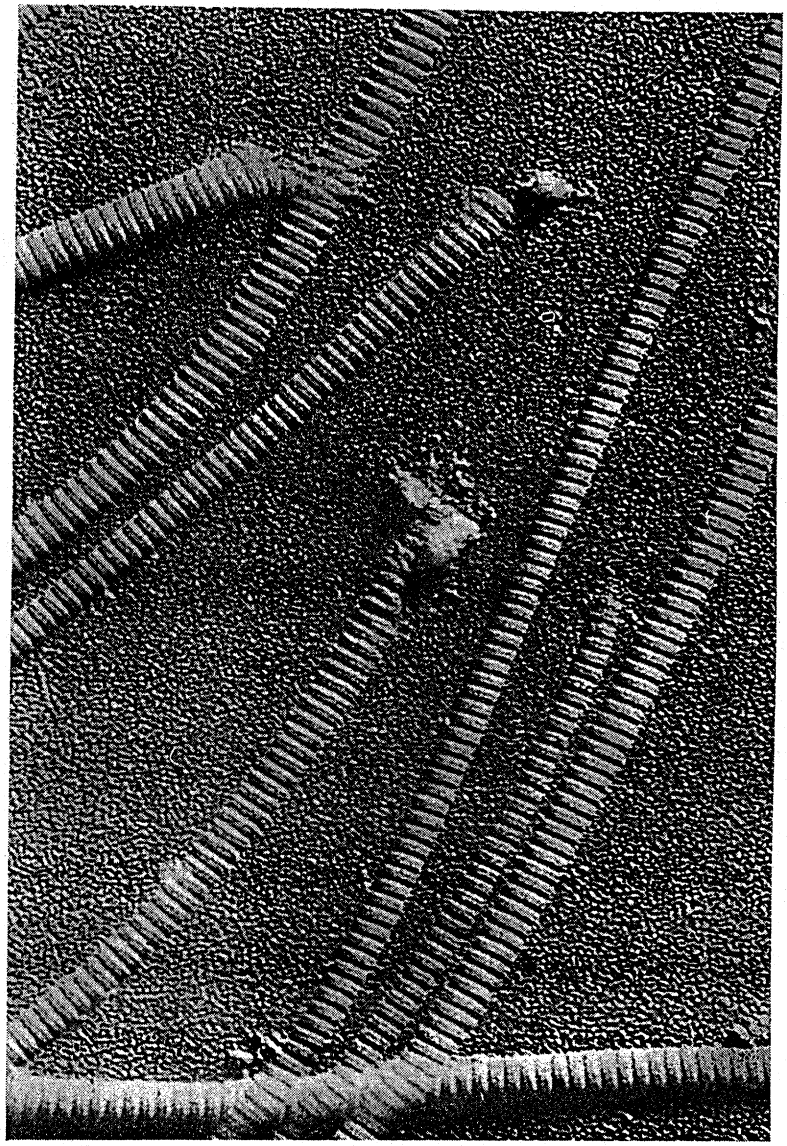

Figure 11. Electron micrograph of cowhide collagen fibrils shadowed with gold. Magnification 30,000 X.

No collagen model consonant with all the observations of diffraction and electron microscopy has been proposed.

Artificial Protein Fibers

We may now turn to a discussion of the structure and properties of the artificial protein fibers. The first consideration is to establish whether globular protein molecules, like those of casein, zein, soybean protein, can be unfolded into extended polypeptide chains. Unfolding has been demonstrated[11] with a dozen globular proteins, and it appears that true fibers can be made from these proteins, i.e., fibering on a molecular scale can be realized. Primary evidence for the conversion from the globular to the fibrous state rests on X-ray diffraction diagrams. Figure 13 shows the pattern produced by

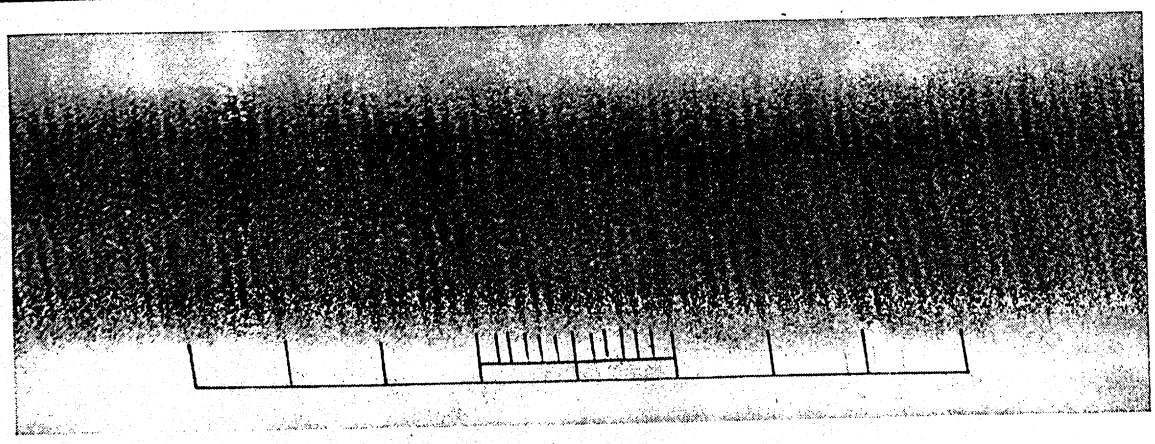

Figure 12. Electron micrograph of cowhide collogen fibrils stained with phospho-tungstic acid. Magnification 200,000 X.

an ovalbumin fiber in which the molecules are largely in the globular form; Figure 14, the pattern after conversion to the fibrous state but without any preferential alignment of the molecular chains; and Figure 15, the same fiber after stretching to orient the chains in the direction of the fiber axis. Marked changes in tensile strength accompany the conversion to the fibrous state. The fiber giving the diffraction pattern of Figure 13 was so weak the brittle that accurate measurement of its strength was impracticable; after conversion to the fibrous state it became pliable and had a strength of about 0.4 gram per denier; upon orientation to give a pattern like that of Figure 15, its strength increased to about 2 grams per denier.

At this point it may be of interest to inquire which of the natural fibers, silk, collagen or wool, we should expect fibers from proteins such as casein, ovalbumin, soybean protein or zein to resemble most closely. From the viewpoint of composition, i.e., the bulkiness and polar nature of a high proportion of the side chains, and the low proline content, we might predict that the polypeptide chains of these proteins will pack more like wool than either silk or collagen. This is, in fact, observed experimentally, for the X-ray pattern of the artificial protein fiber of Figure 15 is practically identical with that of stretched wool (β-keratin). In this connection it should be mentioned that none of the artificial protein fibers have given an α-keratin pattern.

Load-Elongation Data

We may investigate further and compare the tensile properties of artificial protein fibers with those of the natural fibers. For this purpose load-elongation diagrams[12] of ovalbumin, horsehair, collagen and silk fibers are presented in Figures 16, 17 and 18. Horsehair and wool are much alike in composition and mechanical behavior, but because of their larger size, horsehair filaments are more convenient to work with. An important variable in any fiber is the degree of orientation of the crystallites or molecular chains along the fiber axis. This is controlled by the amount of stretch given the fiber after it has been formed. In Figure 16, this is designated by the relative length (R.L.) of the fiber—the ratio of length after stretching to the original lengh. R.L. = 1 designates an unstretched ovalbumin fiber which gives an X-ray pattern corresponding to Figure 13. It is not surprising that this fiber possesses low tensile strength in view of its low orientation; indeed, the orientation is such that the fiber does not withstand stress sufficient to straighten the chains in the less-ordered regions and thus permit elon- the R.L., and thereby the orientation, of the fiber increases, both the elongation and the strengh improve. The elongation passes through a maximum of about R.L. = 2, reaching a value of 35 per cent. Highly oriented fibers represented by R.L. = 6.5 show high strength but lower extensions-at-break; most of the kinks and

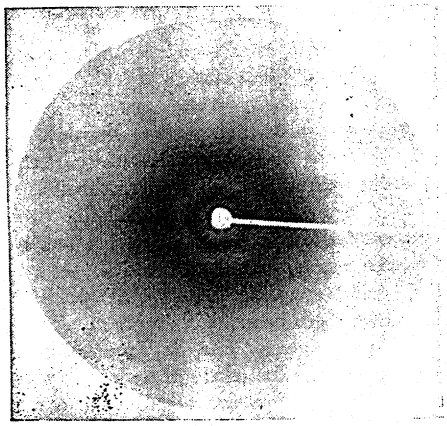

Figure 13. Diffraction pattern of an ovalbumin fiber in which the molecules are largely in the globular form.

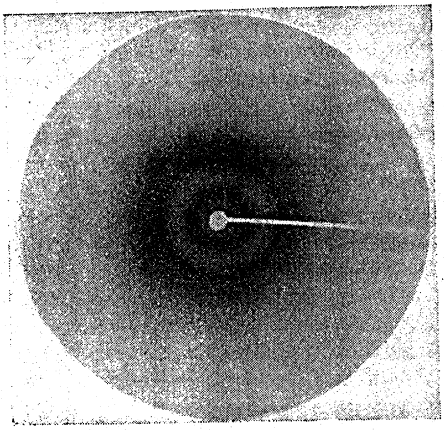

Figure 14. Diffraction pattern of an ovalbumin fiber in which the molecules are unfolded but not oriented.

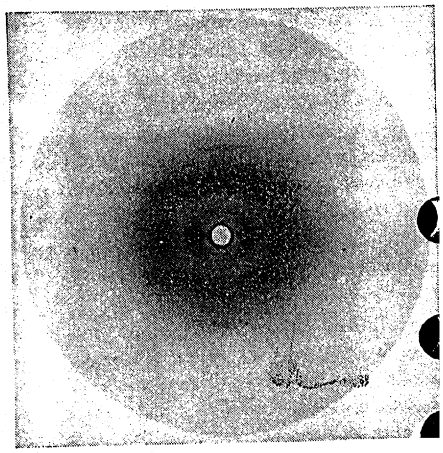

Figure 15. Diffraction pattern of stretched ovalbumin, β-keratin structure.

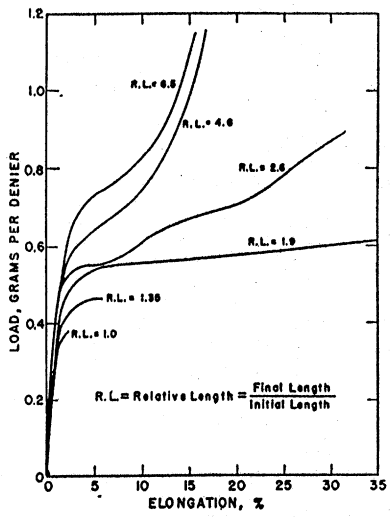

Figure 16. Load-elongation curves of ovalbumin fibers.

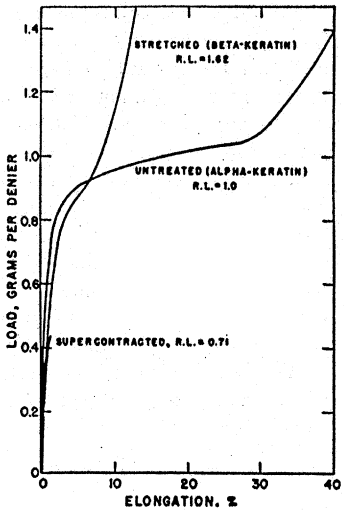

Figure 17. Load-elongation curves of horsehair.

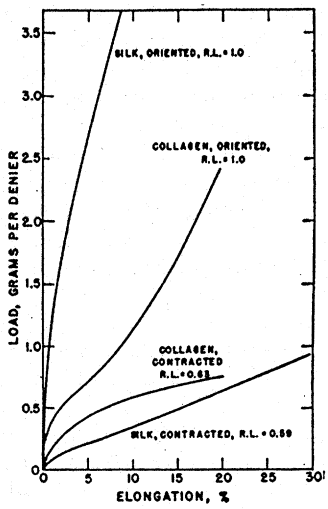

Figure 18. Load-elongation curves of silk and collagen.

the folds were taken out of the molecules in the orientation process.

With increase in relative length beyond R.L. = 1.35, there is a decrease in flexibility, as measured by the knot strength of the fiber or by the ratio of the knot strength to the straight-pull tensile strength. This effect, which is also shown by stretched horsehair, may be a property of the oriented β-keratin structure, or it may be associated with a low effective chain length, since silk which possesses a similar structure retains high flexibility.

Data on horsehair, a typical keratin, are presented in Figure 17. In this case we have three states of orientation: untreated horsehair in the folded α-keratin structure, stretched horsehair in the β-keratin configuration giving an X-ray pattern comparable to highly oriented ovalbumin fibers, and "supercontracted" horsehair giving an X-ray pattern much like that of ovalbumin of R.L = 1—orientation has been destroyed by allowing stretched horsehair to contract to about 30% of its initial unstretched length in boiling buffer solution of pH 8. The stress-strain diagrams corresponding to supercontracted and stretched horsehair roughly parallel the diagrams of ovalbumin with R.L. = 1 and R.L. = 6,5, respectively. Ovalbumin of R.L. = 3 most closely resembles normal horsehair in its stress-strain behavior; horsehair elongates at the expense of the folded structures in both the disorganized and organized regions while in ovalbumin fibers only the disorganized regions can contribute. Both fibers show regions of low modulus associated with chain unfolding, and probably chain slippage, followed by a region of higher modulus associated with increased molecular orientation in the disorganized regions.

Both silk and collagen likewise show considerable dependence in their tensile properties upon the degree of orientation, as shown by the stress-strain curves given in Figure 18. The silk and collagen used in these experiments were suture material and were obtained as highly oriented fibers. R.L. = 1 refers to this oriented state. A lower state of orientation was induced in silk by contraction in 8.42 M HCl at room temperature, and in collagen by contraction in water at 70° C. Oriented collagen has a stress-strain curve of the same general form as highly oriented ovalbumin and horsehair, but has a much higher ultimate strength. Contraction of collagen results in a much lower tenacity, but not in the increased elongation which might be expected from a folded structure. Evidently the weakening effect of disorientation permits the fiber to break before the molecules are fully extended. This effect is even more pronounced in supercontracted horsehair.

Oriented silk, the normal form of silk, differs in its stress-strain behavior in that it shows no well-defined break in its curve. The relatively higher lateral forces between chains resulting from their close lateral packing is reflected in the steep slope of the stress-strain curve at low elongations. That is, a greater force is required to extend silk than is required by a keratin or ovalbumin fiber of the same diameter—silk is a stiffer fiber. Contraction of the silk by acids disorients the crystallites greatly, as demonstrated by the diffraction pattern, but the crystallinity is not destroyed to the degree that it is in contracted collagen or supercontracted horsehair. The disorientation and disordering result in a softer fiber with increased elongation.

Although the ultimate strength and elongation and the shape of the entire stress-srain curve are imporant considerations in any textile fiber many of the properties of a fabric must be determined by the behavior of its fiber at low elongations, for in a fabric the elongation of the individual filaments is never great. Ray[12] has developed this idea and has compared the elastic properties of several fibers at one and two per cent extension. Some of his data are reproduced in Table 1. In addition to the elastic modulus, the rigidity modulus, or the resistance of the fiber toward deformation by torsion, is given. It is to be noted that while all the fibers have nearly the same resistance to twisting, they differ widely in their elastic modulus. They also differ in the amount of work expended in stretching the fiber, which is recovered when the stress is removed. This property is related to the resilience of the fiber, and wool is exceptional among the natural fibers in this

TABLE 1*

Fiber	Rigidity Modulus G (dynes/cm.²)	Elastic Modulus E (dynes/cm.²)	E/G	Work Recovery at Elongation of 1%	2%
Wool	1.7 x 10^{10}	3.4 x 10^{10}	2.0	95%	90%
Casein	1.3	2.9	2.2	92	65
Silk	1.2	13.9	11.5	75	45
Cellulose	1.4	5.0	3.5	50	20
Cellulose, high tenacity	1.6	17.1	10.5	..	..

* L. G. Ray, Jr., Textile Research Journal *17*, 1 (1947).

respect. Casein bears a remarkable resemblance to wool in moduli as well as work recovery, showing that it is more wool-like than silk-like in its elastic properties at low elongations. At higher elongation casein and ovalbumin recover less completely both in respect to length and work than does wool or silk.

So far we have considered the tensile properties of fibers at water contents corresponding to standard testing conditions (65% R.H. and 70° F.). In the wet state, the artificial protein fibers lose considerable strength and are in marked contrast to wool and silk in this respect. It has already been stated that the high wet strength of wool depends largely on the presence of primary bonds between chains formed by cystine linkages. In silk, the high proportion of crystalline regions provide anchor points along the polypeptide chains maintaining the strength of the fiber in the wet condition. The crystallinity of the artificial protein fibers produced so far is insufficient to confer adequate wet strength, and it has been necessary to employ various "hardening" treatments, such as reaction of the fibers with formaldehyde or quinone, to stabilize the fibers through the formation of cross-linkages between chains. It is noteworthy, however, that ovalbumin fibers giving X-ray patterns like Figure 13 have wet strength that is half the dry strength without any hardening treatment. Casein fibers are much lower on the crystallinity scale and attain appreciable wet strengths only after hardening.

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